



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<p>(21) International Application Number: <b>PCT/FI98/00666</b></p> <p>(22) International Filing Date: <b>26 August 1998 (26.08.98)</b></p> <p>(30) Priority Data: <b>973501</b> <b>26 August 1997 (26.08.97)</b> <b>FI</b></p> <p>(71) Applicant (for all designated States except US): <b>SOHKAR OY [FI/FI]; Kyllikinportti 2, FIN-00240 Helsinki (FI).</b></p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): <b>KUUSISTO, Juhani [FI/FI]; Pekolanraitti 6 B 3, FIN-30100 Forssa (FI). LINDQVIST, Irma, Christina [FI/FI]; Niittypolku 18, FIN-02460 Kantvik (FI). ANTILA, Juhani [FI/FI]; Jääskentie 3 B, FIN-02140 Espoo (FI).</b></p> <p>(74) Agent: <b>KOLSTER OY AB; Iso Roobertinkatu 23, P.O. Box 148, FIN-00121 Helsinki (FI).</b></p>		<p>(81) Designated States: <b>AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, EE (Utility model), ES, FI, FI (Utility model), GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).</b></p> <p><b>Published</b> <i>With international search report.</i></p>
<p>(54) Title: <b>A RAW MATERIAL FOR USE IN THE PREPARATION OF PECTIN AND RELATED COMPOUNDS, AND A METHOD FOR THE PREPARATION OF SAME</b></p>		
<p>(57) Abstract</p> <p>The invention relates to a raw material for use in the preparation of pectin and related compounds, the raw material being pressed, stabilized sugar beet pulp subjected to biotechnical pre-treatment. In accordance with the invention the raw material is prepared by pre-treating fresh pressed sugar beet pulp by lowering the pH to a value between 3.5 and 4.5 (preferably 3.9 and 4.3) and subsequently storing the obtained acid pulp in tight, i.e. substantially oxygen-free conditions.</p>		

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## **A RAW MATERIAL FOR USE IN THE PREPARATION OF PECTIN AND RELATED COMPOUNDS, AND A METHOD FOR THE PREPARATION OF SAME**

The invention is related to an improved method for the preparation of organic materials, such as pectin, from sugar beet pulp, from which sugar  
5 has been extracted. In accordance with the invention, said sugar beet pulp, from which sugar has been extracted, is pre-treated in a biotechnical process in mildly acidic, deoxidizing conditions prior to hydrolysis or extraction of the desired products. In the biotechnical process the fresh pulp is subjected a de-  
10 oxidizing, mildly acidic pre-treatment, and the pulp is allowed to stabilize in substantially oxygen-free conditions. The stabilized pulp, which is stable for months in air-tight storage, is used as a raw material in the preparation of sugar beet pectin and related products, such as araban, arabinose, galactan and ferulic acids.

### **DESCRIPTION OF THE PRIOR ART**

15 Sugar beet hemicellulose is a complex hydrocolloid based on galacturonic acid polymers, the backbone polymer chain comprising regions composed of rhamnose and galacturonic acid for connecting polygalacturonic acid units. Araban and galactan polymer chains are connected to the rhamnose units in these hairy regions.

20 A galacturonic acid chain is partly acetylated and methylated. Xylose and ferulic acid units are present in the side chains. Pectin can be extracted from sugar beet pulp after mild acid hydrolysis. The composition of pectin depends on the extraction conditions. Some pectic substances, such as arabans, can be alternatively extracted after alkaline hydrolysis. In his patent  
25 (US 5,008,254), Michael Weibel describes processes for carrying out the hydrolysis in acid conditions (pH below 4.5) or in alkaline conditions (pH over 9.0) at elevated temperatures.

WO 97/30215 (Wong, E., et al.) discloses use of fermented sugar beet pulp for making paper or cardboard. The preparation of pectin and related  
30 compounds is not disclosed.

A conventional process for the preparation of sugar beet pectin is by acid hydrolysis at a pH of about 1.5, followed by neutralization, purification by filtration and precipitation of the pectins with alcohol. McCleary et al. disclose an improved method of preparing araban from fresh sugar beet pulp by  
35 extraction with an alkaline lime solution (US 5,250,306). Schiweck et al. pre-

pared L-arabinose from sugar beet araban or beet pulp by hydrolysis in alkaline conditions (US 4,816,078).

The raw material for pectins has been either fresh or dried pulp. Fresh pulp is available only for a short period during the sugar beet season.

5 Consequently, dried pulp has usually been employed.

#### ADVANTAGES OF THE INVENTION

The use of fresh pulp in the preparation of pectins is not economically feasible due to its limited availability. On the other hand, when the pulp is dried, reactions occur causing colour formation, lower quality of the products  
10 obtained from the pulp, and reduced pectin yield. In practice no suitable raw material for sugar beet pectin has been found, and consequently the production and use of this excellent plant hydrocolloid has remained very low.

It has now been discovered that the use of non-dried sugar beet pulp, from which sugar has been removed and which has been subjected to  
15 biotechnical pre-treatment in acidic, deoxidizing conditions, results in an improvement in the total process increasing the yields of the desired products from the raw material, which remains stable in storage and is available throughout the year. In the pre-treatment the free sugars still present in said pulp, from which sugar has been removed, are oxidized into organic acids and  
20 oxygen is removed, but the pectic substances are not affected. Kept away from light in tight storage, i.e. in substantially oxygen-free conditions, the treated pulp remains stable for months. This stable pulp is an excellent raw material in the preparation of sugar beet pectin and related compounds, such as araban, galactan, L-arabinose, ferulic acids, L-rhamnose, etc.

#### 25 DESCRIPTION OF THE INVENTION

Fresh, pressed sugar beet pulp, from which sugar has been extracted and whose dry substance content is about 20 to 25 percent by weight, is pre-treated by reducing its pH to about 4, preferably by mixing the pulp with  
30 a suitable acid solution. Organic acids, such as formic acid, lactic acid, acetic acid and/or mixtures thereof are effective and easy to use. Commercially available acid mixtures include e.g. "Ensimax", which consists of formic acid and lignosulphonate, and silage (AIV) acid consisting mainly of formic acid. The choice of acid depends on the price and pre-treatment conditions. Very volatile acids, such as formic acid, can cause irritation if used without proper  
35 protection. The lime content of the pressed pulp is preferably low, i.e. no lime

or aluminium is added to the beet pulp (the cossette) to facilitate the pressing at the final stage of the sugar (saccharose) separation process. After the pressing the temperature of the pulp is about 60°C and pre-treatment is carried out preferably immediately after the pressing before the pulp cools off.

5           The pre-treated pulp having a pH of about 4 is preferably packaged in air-tight storage and allowed to stabilize. The tight storage can be e.g. a plastic bag or tube made of polyethene, or what is known as a flat silo. The protection prevents light and air (oxygen) from accessing the treated pulp. The enzyme activity of lactic acid bacteria present in the fresh pulp causes oxidation of free sugars during the stabilization. Organic acids, mainly lactic acid, are formed. The deoxidizing reaction with acid formation as a result removes oxygen and free sugars from the material and prevents further fermentation of the pulp. The obtained pulp, preferably having a pH of 3.5 to 4.5 (most preferably 3.9 to 4.3) and 20 to 27 percent by weight of dry substances, is stored  
10           air-tightly at a non-elevated temperature, where it is stable for at least a year. The concept "air-tightly" refers to the pulp being stored in e.g. plastic bags or tubes having a volume of 50 to 200 m<sup>3</sup>, or a sealed flat silo.

          Said stable pulp is preferably prepared from pulp which has been pressed without lime or aluminium addition. The composition of stable pulp is  
20           typically: cellulose and lignin about 30 percent by weight, hemicellulose about 70 percent by weight, of which a third is pectin, pH about 4. This raw material is available throughout the year, its preparation is inexpensive and storage easy. The composition of the raw material is advantageous since it does not include low molecular weight sugars, saccharose or glucose.

## 25   EXAMPLES

### Example 1. Preparation of pectin

          Fresh pressed pulp with no addition of lime and with a dry substance content of about 22% was contacted with a commercial acid mixture "Ensimax" (manufacturer: Kemira Oy, Finland); 4 litres of acid mixture per 1  
30           ton of pressed pulp. Said acid mixture contained 30 percent by weight of formic acid (85%), 20 percent by weight of acetic acid (80%) and 50 percent by weight of lignosulphonate (37%). During mixing the temperature of the pulp was 50 to 60°C and it was mixed for about 1 minute in a screw mixer. The mixture was packaged in a tight plastic bag made from 0.25 mm polyethene  
35           film. The inner surface of the film was black and the outer surface white, pro-

viding efficient protection for the pulp against light and oxygen. The pulp was allowed to cool off and stabilize outdoors and the bags were stored in an outdoor storage.

5 The treated pulp, which had been stored for about 6 months, was used as raw material for sugar beet pectin. The composition of the pulp was as follows: 25 percent by weight of dry substance, Ensimax 0.4 percent by weight, free sugars below 1 percent by weight. Acid hydrolysis was performed first: pH 1.5, temperature 70°C. The hydrolysate was neutralized with sodium carbonate to pH 3, and the solution was separated from insoluble pulp by a  
10 decanting centrifuge and filtered by what is known as precoat filtration in the presence of a filtration additive. The filtered solution was concentrated by evaporation below 60°C to a dry substance content of 9 percent by weight. Pectin was precipitated from the concentrated solution by addition of isopropanol so that the solution contained 75 percent by weight of isopropanol. The  
15 precipitated pectin was washed with a 60% isopropanol solution, separated by centrifugation and dried in an air current at 50°C. The yield was 15 percent by weight of pectin of pulp dry substance.

#### Example 2. Preparation of araban

20 Fresh pressed pulp was pre-treated as in Example 1 and the pre-treated stable pulp was taken out of storage after 8 months. The pulp was hydrolyzed at pH 12, temperature 95°C, by addition of milk of lime. The hydrolysate was neutralized with carbon dioxide and the pulp was separated from the solution by a filter press. After concentration the araban in the filtrate was separated from salts and other substances by chromatography using a poly-  
25 styrenedivinylbenzene separation resin. The araban fraction was evaporated and dried. The yield of crude araban was 20 percent by weight.

#### Example 3. Preparation of L-arabinose

30 Fresh pressed pulp was pre-treated as in Example 1 and the stable pulp was taken from storage after 7 months. The pulp was hydrolyzed with milk of lime as in Example 2, neutralized, and filtered. The solution was then concentrated by evaporation and the araban was hydrolyzed into L-arabinose by addition of sulphuric acid to pH 0.8 and by heating to 90°C. The hydrolyzed solution was neutralized with sodium hydroxide to pH 6 and the sulphate precipitate formed in the neutralization was removed by filtration. The arabinose  
35 fraction was separated by chromatography using a polystyrenedivinylbenzene separation resin in Na form. The arabinose solution was further purified with

cation and anion exchange and a colour removal resin (Optipore) and evaporated, whereby the L-arabinose was crystallized. The crystals were separated from the mother liquor by centrifugation. The yield was about 15 percent by weight of L-arabinose of pulp dry substance.

5            Example 4. Preparation of araban and arabinose

          Fresh pressed pulp was treated and pectin was precipitated with isopropanol as in Example 1. Free L-arabinose and arabinogalactan-polysaccharide remained in the filtrates and washing solutions generated in the preparation of pectin. Isopropanol was removed from the solution by distillation; whereupon the polysaccharides were separated by chromatography from the L-arabinose using a separation resin either directly or after acid hydrolysis of the arabinogalactan polymers performed to increase the L-arabinose content. The L-arabinose was crystallized from the monosaccharide fraction as in Example 3 and the araban was prepared by purification and drying from the non-hydrolyzed polymer fraction as in Example 2.

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## CLAIMS

1. A raw material for use in the preparation of pectin and related compounds, **characterized** by being purified, stabilized sugar beet pulp subjected to biotechnical pre-treatment.
- 5 2. A raw material as claimed in claim 1, which has a pH of 3.5 to 4.5 (preferably 3.9 to 4.3) and 20 to 27 percent by weight of dry substance, and is substantially free from fermentable sugars and has been stored in substantially oxygen-free storage.
- 10 3. A method for the preparation of a raw material for use in the preparation of pectin and related compounds, **characterized** by pre-treating fresh pressed sugar beet pulp by lowering the pH to a value between 3.5 and 4.5 (preferably 3.9 and 4.3) and storing the acid pulp in substantially oxygen-free conditions.
- 15 4. A method of utilizing biotechnically pre-treated sugar beet pulp in the preparation of pectin and related compounds, **characterized** by fresh sugar beet pulp, from which sugar has been extracted, being pre-treated by lowering the pH of the pulp to 3.5 to 4.5 (preferably about 4) and by the acidified pulp being stored air-tightly for removal of oxygen and free sugars in an induced biotechnical reaction, whereupon the pulp is stored in tight sub-  
20 stantially oxygen-free conditions.
5. A method as claimed in claim 4, **characterized** by the use of pressed pulp with no addition of lime or aluminium.
6. A method as claimed in claim 5, **characterized** in that the pH is lowered by mixing a suitable acid or acid mixture with the pressed pulp.
- 25 7. A method as claimed in claim 6, **characterized** in that the acid or acid mixture is mixed into pulp at a temperature of about 60°C, preferably 50 to 60°C, i.e. preferably immediately after the pressing.



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00666

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08B 37/06, D21C 3/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08B, D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI, CAPLUS

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 8403286 A1 (BATTELLE MEMORIAL INSTITUTE), 30 August 1984 (30.08.84) --	1-7
A	WO 9730215 A1 (ERIDANIA BEGHIN-SAY), 21 August 1997 (21.08.97) --	1-7
A	STN International, File CAPLUS, CAPLUS accession no. 1983:33388, Prikryl, Jaroslav et al: "Use of preservatives in agriculture. III. Use of silko in the preservation of green forage and sugar beet pulp"; & Agrochemia (Bratislava) (1982), 22(10), 297-9 --	1-7



Further documents are listed in the continuation of Box C.



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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>STN International, File CAPLUS, CAPLUS accession no. 1980:109374, Gerbut, A. Ya. et al: "Characteristics of storage of highly pressed beet pulp"; &amp; Sakh. Prom-st. (1980), (1), 30-3</p> <p>-- -----</p>	1-7

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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WO 9730215 A1	21/08/97	AU 1728097 A AU 7499996 A FR 2744735 A,B NO 983695 A	02/09/97 22/08/97 14/08/97 12/08/98

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